(12) UK Patent Application (19) GB (11) 2 239 654 (13) A

(43) Date of A publication 10.07.1991

(21) Application No 9100148.7

(22) Date of filing 04.01.1991

(30) Priority data
(31) 461152 (32) 05.01.1990 (33) US

(71) Applicant
Brown & Williamson Tobacco Corporation

(Incorporated in the USA - Kentucky)

1500 Brown & Williamson Tower, Louisville Galleria,
P O Box 35090, Louisville, Kentucky 40232,
United States of America

(72) Inventors
Frank Kelley St Charles
John Harvey Lauterbach
Li-Chung Chao
Jiunn-Yann Tang
Baran B Chakraborty
Andrew McMurtrie

(74) Agent and/or Address for Service
K J H MacLean
British-American Tobacco Company Limited,
Group Research and Development Centre,
Regent's Park Road, Southampton, SO9 1PE,
United Kingdom

(51) INT CL[5]
C09B 67/44, A23G 3/32, C09B 61/00

(52) UK CL (Edition K)
C4P P112
A2B BSX B809 B819
A2C CEFA
C2S SEX S106 S300 S309 S313 S319
C3U UCA UCC U219
U1S S1116

(56) Documents cited
GB 1082284 A EP 0264873 A US 3769041 A
US 2651576 A

(58) Field of search
UK CL (Edition K) A2B BSC BSX BW, A2C CEFA, C4P PE
INT CL[5] A23G, A24C, C09B
WPI: CLAIMS

(54) **Caramel composition for dyeing cigarette paper; purification of caramel**

(57) An aqueous dye composition for colouring cigarette paper brown comprises caramel as the brown colouring agent, and a plasticiser to prevent the paper from becoming brittle, e.g. glycerine, propylene glycol, polyethylene glycol or triethylene glycol. The composition can further include (a) carmine as a red colouring agent to change the shade and hue of the brown colour of the caramel; and (b) a burn additive to promote the burning of the dyed paper, e.g. potassium citrate.

Caramel is purified by triturating with aqueous ethanol or by diafiltration to remove most of the compounds in the caramel which will pass through a dialysis membrane having a molecular weight cut-off range of 2000-30,000.

GB 2 239 654 A

FIG. 1

Flow Scheme for Membrane Ultrafiltration of Caramel

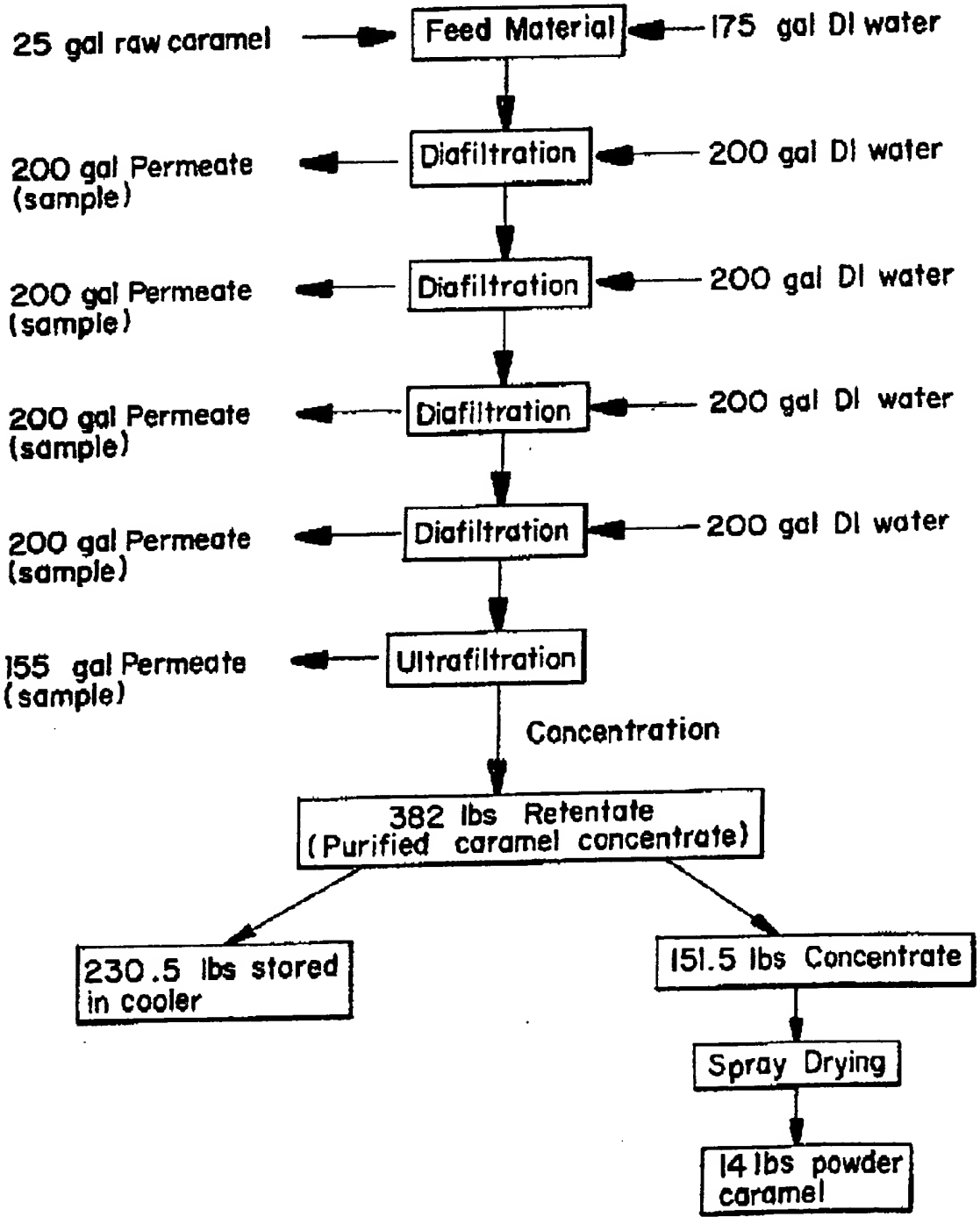
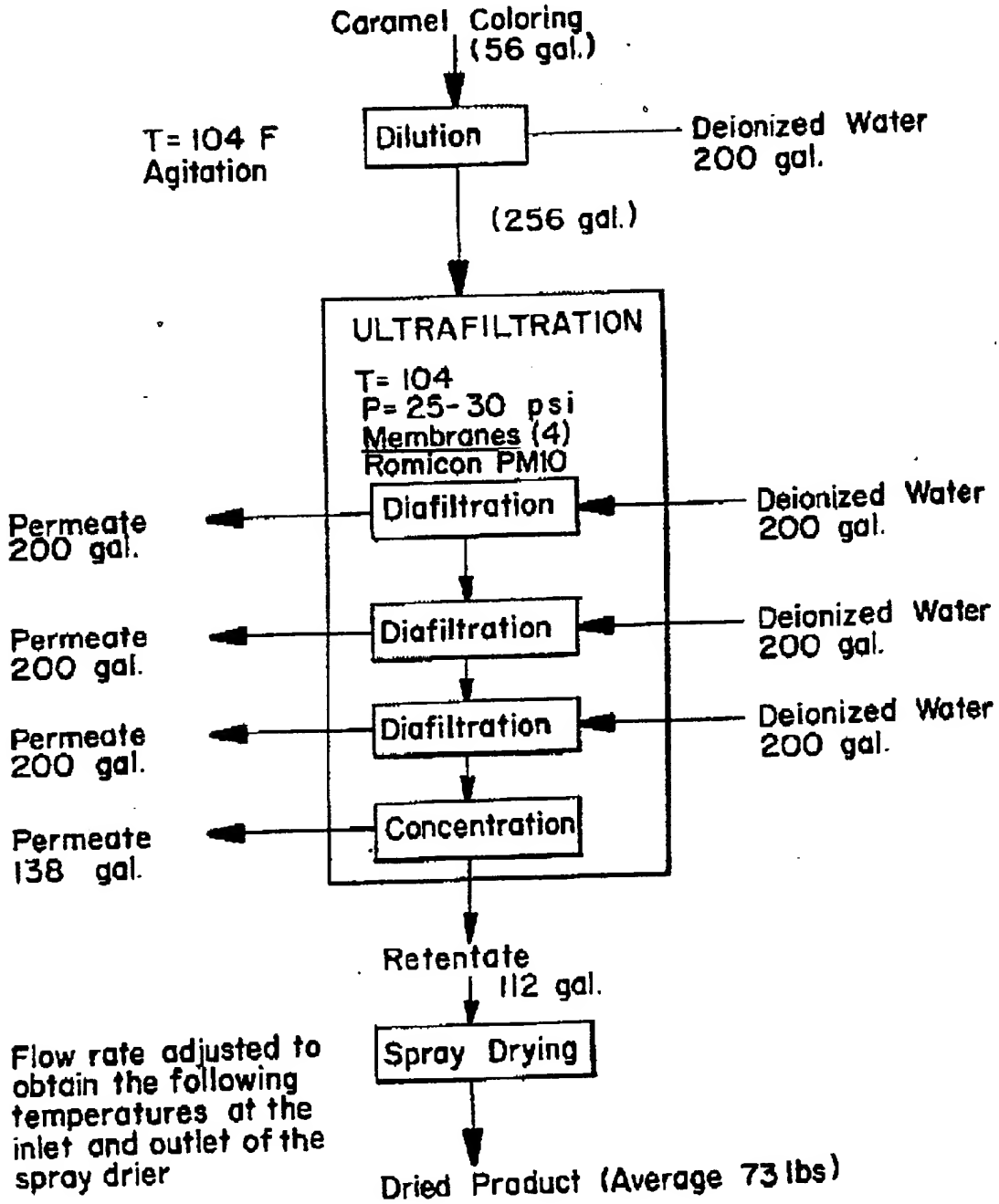


FIG. 2

Flow Diagram for Processing of 400 gallons Caramel Color



2239654

A Dye for Colouring Cigarette Paper

The present invention relates to dyes, and more particularly to a dye for colouring cigarette paper.

It is known to colour cigarette wrapper paper with synthetic dyes. However, acceptable commercially available papers usually incorporate synthetic materials which in many instances are unacceptable for taste or other reasons.

It is an object of the present invention to provide a dye using natural materials as opposed to synthetic materials as the colouring agent. It is another object of the present invention to provide a dye using natural materials which have chromophores at an intensity closely approximating chromophores of synthetic dyes. It is even another object of the present invention to provide a dye using natural materials as the colouring agent which does not make the cigarette paper brittle.

The present invention provides cigarette wrapper paper colouring dye comprising caramel, a plasticiser to prevent the paper from becoming brittle, and water.

One advantageous embodiment of the dye of the present invention comprises from about 3 to about 20 weight per cent caramel, from about 2 to about 8 weight per cent glycerine, and from about 72 to about 95 weight per cent water.

Another advantageous embodiment of the dye of the present invention comprises from about 3 to about 20 weight

per cent purified caramel, from about 1.0 to about 10 weight per cent 2X carmine solution, from about 2 to about 8 weight per cent glycerine, and from about 62 to about 94 weight per cent water.

Yet another advantageous embodiment of the dye of the present invention comprises from about 3 to about 20 weight per cent caramel, from about 1.0 to about 10 weight per cent 2X carmine solution, from about 2 to about 8 weight per cent glycerine, from about 3 to about 9 weight per cent potassium citrate, and from about 53 to about 91 weight per cent water.

The present invention further provides a process for purifying caramel extract. The present invention also further provides a smoking article product utilising a caramel coloured rod wrapper.

A better understanding of the present invention will be had upon reference to the following discussion in conjunction with the accompanying drawings wherein:

Figure 1 is a flow diagram of one process used to purify caramel extract; and,

Figure 2 is a flow diagram of a modified process used to purify caramel extract.

Caramel is defined by 21 Code of Federal Regulations, section 73.85 (April 1, 1988) as follows:

(a) Identity: (1) The colour additive caramel is the dark-brown liquid or solid material resulting from the carefully controlled heat treatm nt of the following food-

grade carbohydrates: Dextrose, Invert sugar, Lactose, Malt syrup (sic), Molasses, Starch hydrolysates and fractions thereof, and Sucrose.

(2) The food-grade acids, alkalis, and salts listed in this subparagraph may be employed to assist caramelisation, in amounts consistent with good manufacturing practice.

(i) Acids: Acetic acid, Citric acid, Phosphoric acid, Sulphuric acid, Sulphurous acid,

(ii) Alkalis: Ammonium hydroxide, Calcium hydroxide U.S.P., Potassium hydroxide, Sodium hydroxide.

(iii) Salts: Ammonium, sodium, or potassium carbonate, bicarbonate, phosphate (including dibasic phosphate and monobasic phosphate), sulphate and sulphite.

(3) Polyglycerol esters of fatty acids, identified in 172.854 of this chapter, may be used as antifoaming agents in amounts not greater than that required to produce the intended effect.

(4) Colour additive mixtures for food use made with caramel may contain only diluents (sic) that are suitable and that are listed in this subpart as safe in colour additive mixtures for colouring foods.

(b) Specifications. Caramel shall conform to the following specifications: Lead (Pb), not more than 10 parts per million; Arsenic (As), not more than 3 parts per million; and, Mercury (Hg), not more than 0.1 part per million.

Preferably, the caramel used as the brown colour agent

in the dye has been purified to remove most of the compounds in the caramel which will pass through a dialysis membrane having a molecular weight cut-off range of from about 2,000 to 30,000. This can be readily accomplished by the diafiltration method or alternatively by triturating the caramel with ethyl alcohol and water. Further, one-tenth per cent solution of the purified caramel powder used in the dye of the present invention has an absorbance in a 1 cm cell of from about 1.20 to about 1.50 at 610 nanometers.

Three samples of caramel colour extract were processed to provide a purified caramel. The following examples discuss processes of each of these three samples.

EXAMPLE I

110 grams of caramel concentrate (55.5% solids) was diluted with deionised water at 6/1 ratio (v:v, water:caramel). The diluted solution was then diafiltered through the membrane with five washes of 700 ml water. The permeate and retentate were collected, and solid content and colour intensity were determined. Results are summarised in Table 1 below.

Two types of hollow fibre membranes with molecular weight cut-offs of 2,000 and 30,000 were used. Results showed that there were no significant differences in colour retention and solid removal (three-fourths of the original solids) between these two membranes. Therefore, it is recommended that the membrane with the 30,000 molecular weight cut-off be selected since flow through the membrane

increases with molecular weight cut-off.

Table 1

Fraction # of Permeate (Vol. ml)		Solid Wt (g)*	% of Total Solids Removed
I	500	17.1	47.1
II	500	9.7	26.7
III	500	4.9	13.5
IV	500	2.6	7.1
V	500	1.2	3.3
VI	400	0.39	1.1
VII	456	0.44	1.2

* Per 100 g of concentrate

The results (Table 1) indicate that approximately 95% of the low molecular weight solids were removed after four 500 ml washes.

200 gram and 300 gram batches with dilution factor of 4/1 and 3.3/1, respectively, were tried and purification efficiencies were as good as that for the 100 gram batch.

Example II

Figure 1 is a flow chart illustrating the following described process.

Twenty-five gallons of caramel colour extract was prefiltered, diluted and ultrafiltered by using hollow fibre membranes with a 10,000 molecular weight cut-off.

The caramel colour xtract was filtered through a 20

micron prefilter to remove particulate matter that could plug the membranes during ultrafiltration. The resulting caramel colour mixture was diluted with 175 gallons of deionised water and ultrafiltered at 40°C and 25-30 psi pressure. A four step diafiltration technique was utilised, and during each step 200 gallons of permeate was removed and 200 gallons of deionised water was added for constant volume filtration. The diafiltered mixture from the fourth step was then concentrated by ultrafiltration to provide 382 pounds of retentate solution. Finally, 151.5 pounds of the concentrate was spray dried in a Niro spray dryer with an inlet temperature of 400°F and an outlet temperature of 200°F providing 14 pounds of purified caramel powder.

The caramel colour extract, each of the 200 gallons permeates, the 155 gallon permeate from the ultrafiltration concentration step, and the purified concentrate were analysed for tinctorial power, soluble solid content, and specific gravity. The results are summarised in Table 2 below.

Table 2

Test Samples	Total Vol(g)	Sp. Gravity	% Solid	Total Solid (Lbs)	Relative Colour Distribution
Raw caramel	25.0	1.260	55.00	144.38	6900
Purified Conc. (Retentate)	44.6	1.030	8.98	34.30	6422
1st Composite Permeate	200.0	1.013	3.99	67.23	418
2nd Composite Permeate	200.0	1.000	1.33	22.11	134
3rd Composite Permeate	200.0	1.000	0.43	7.15	39
4th Composite Permeate	200.0	1.000	0.13	2.16	20
Permeate from Concentration	155.0	1.000	0.22	2.84	213

With reference to Table 2 above, it was determined that since about 98% of the removable solids was collected in the first three fractions of the permeate that it would be feasible to reduce the number of ultrafiltration steps from four to three.

Example III

Figure 2 is a flow chart illustrating the following

described process.

Fifty six gallons of caramel colour extract was prefiltered, diluted, and ultrafiltered by using Romicon PM10 hollow fibre membrane cartridges (10,000 molecular weight cut-off range).

The caramel extract was filtered through a 20 micron prefilter to remove any particulate matter that could plug the membranes during the following ultrafiltration. The resulting caramel colour mixture was diluted with 200 gallons of deionised water and ultrafiltered at 40°C and 25-30 psi pressure. A three step diafiltration technique was utilised, and during each step 200 gallons of permeate was removed as 200 gallons of deionised water was added for constant volume filtration. Three successive diafiltration steps were performed. The final diafiltrated mixture was concentrated to 112 gallons and was spray dried as in Example II to provide 73 pounds of purified caramel powder.

Caramel colourants are characterised by the tinctorial power and colour hue index. These are obtained by measuring the colour absorbance at 610 nm and 510 nm through a 1 cm cell. The absorbance of all purified caramel samples obtained from Examples I, II, and III were determined. The results (Table 3) show that a homogeneous purified caramel with good colour quality was produced from the process of each example.

Table 3

Colour Hue-Index of Various Purified Caramel Samples

Purified Caramel Samples	Absorbance of 0.1% W/V 610nm	510nm	Colour Hue Index*
From Example III, (Figure 2)			
Composite #1	1.480	3.640	3.91
Composite #2	1.476	3.634	3.91
Composite #3	1.466	3.610	3.91
From Example II, (Figure 1)	1.470	3.548	3.83
From Example I, (30,000 MW cut-off)	1.372	3.430	3.98
From Example I, (2,000 MW cut-off)	1.442	---	---

* Colour hue index (1/microns)=log $(A_{510}/A_{610})/(0.61u-0.51u)$

A preferred plasticiser used in the dye is glycerine. However, other plasticisers such as, for example, propylene glycol, polyethylene glycol, triethylene glycol, and the like can be used.

A red colouring agent, preferably carmine, or a water based solution of carmine can also be incorporated in the dye to change the shade and hue of the brown colour of the caramel. Carmine is made from the scale insect Coccus cati L., Homoptera, commonly known as cochineal. A suitable

water based carmine solution is marketed by Crompton and Knowles Corp., 1595 MacArthur Blvd., Mahwah, New Jersey, under the trademark "CARMISOL". For example, a 2X carmine solution was used in the dye which is a solution of carmine containing 7% active carmine.

Example IV

Four carmine samples were obtained from Crompton & Knowles Corporation (C&K) for evaluation. The colour strength of these samples was determined by measuring the absorbance at 528 nm using 0.01% W/V solution as compared to a sample of freeze dried beet extract. Results are summarised as follows:

Table 4

Sample Red Dye	Absorbance at 528 nm (0.01% W/V)
1. L-2665 carmine powder	1.0899
2. 50-272010-00 carmine solution	0.4570
3. 50-272015-00 carmine solution	0.7465
4. 50-272020-00 carmine solution	0.4700
Beet Extract (freeze-dried)	0.0325

Based on the absorbance, carmine powder (L-2665) was found to be the best among the samples tested.

During the development of brown dye formulation using the purified caramel and carmine powder, small carmine particles were found suspended in the dye solution which caused speck problems on the paper. It was suspected that the pH of the ink solution may be one of the crucial factors in obtaining a homogeneous solution. Test results indicated

that the speck problem could be alleviated by adjusting the pH of ink solution from 5.7 to 8.6. In addition to 7% active red dye, the preferred carmine solution (referred to as carmine 2X) contains glycerine and potassium hydroxide.

In addition, typical cigarette wrapper paper includes a filler which is basic, such as calcium carbonate. Therefore, the dye can also include a pH adjusting agent to adjust the pH of the dye to from about 5.0 to about 10.5, and preferably about 8.6.

One such pH adjuster which works well in the dye of the present invention is potassium hydroxide. However, other basic salts and hydroxides may also be used.

Depending upon the cigarette burn rate desired, a burn rate enhancer or burn additive may have to be included in the dye. One appropriate burn additive is potassium citrate. However, other burn rate additives known in the art may also be used, such as, for example sodium and potassium salts of carboxylic acids such as citric, acetic, tartanic, malic, propionic, caprylic, etc; ammonium phosphate; carbonates; and the like.

CLAIMS

1. A cigarette wrapper paper colouring dye comprising: caramel, a plasticiser to prevent the paper from becoming brittle, and water.
2. The dye of Claim 1, and further comprising carmine.
3. The dye of Claim 1 or 2, and further comprising a burn additive.
4. The dye of Claim 3, wherein the burn additive comprises potassium citrate.
5. The dye of any one of Claims 1 to 4, wherein the plasticiser comprises glycerine.
6. The dye of any one of the preceding claims, and further comprising a pH adjusting additive to adjust the pH of the dye to between about 5.0 and about 10.5.
7. The dye of Claim 6, wherein the pH additive comprises potassium hydroxide.
8. The dye of any one of the preceding claims, wherein the caramel comprises purified caramel.
9. The dye of Claim 8, wherein the caramel was purified by diafiltration and is the resulting retentate.
10. The dye of Claim 9, wherein the resulting caramel retentate comprises no more than 30% of the mass of the unpurified caramel.
11. The dye of Claim 9 or 10, wherein the caramel retentate is the material retained when passing untreated caramel through a membrane designated to have a molecular weight cut-off of from 2,000 to 30,000.

12. The dye of Claim 9, wherein 0.1% solution of the purified caramel has an absorbance of from about 1.20 to 1.50 at 610 nanometers using a 1 cm cell.

13. The dye of Claim 8, wherein the caramel is purified by triturating the caramel with ethyl alcohol and water.

14. The dye of any one of Claims 2 to 13, wherein the carmine solution comprises from about 1.0% to 10% by weight of the dye.

15. A cigarette wrapper paper colouring dye comprising; from about 3 weight per cent to about 20 weight per cent purified caramel, from about 2 weight per cent to about 8 weight per cent glycerine, and from about 72 weight per cent to about 95 weight per cent water.

16. The dye of Claim 15, and further comprising from about 1.0 weight per cent to about 10.0 weight per cent carmine solution.

17. The dye of Claim 15 or 16, and further comprising from about 3 weight per cent to about 9 weight per cent potassium citrate.

18. The dye of Claim 15, 16 or 17, and further comprising a pH adjusting additive to provide a pH of from about 5.0 to about 10.5.

19. A process for purifying caramel colour comprising the steps of prefiltering the caramel colour extract to remove particulate matter above a predetermined size, diluting the resulting prefiltered extract, as permeate is removed by the diafiltering step, adding a volume of

deionised water to the diafiltering step equal to the volume of permeate removed to provide a resulting retentate, and spray drying the resulting retentate to provide a purified caramel powder product.

20. A cigarette product comprising a tobacco rod, said tobacco rod being circumscribed by a paper wrapper having a dye therein comprising caramel, a plasticiser to prevent the wrapper from becoming brittle, and water.

21. The product of Claim 20, said dye further comprising carmine.

22. The product of Claim 20 or 21, said dye further comprising a burn additive.

23. The product of Claim 20, 21 or 22, wherein the burn additive comprises potassium citrate.

24. The product of Claim 20, 21, 22 or 23, wherein the plasticiser comprises glycerine.

25. The product of any one of Claims 20 to 24, said dye further comprising a pH adjusting additive to adjust the pH of the dye to between about 5.0 and about 10.5.

26. The product of Claim 25, wherein the pH additive comprises potassium hydroxide.

27. The product of any one of Claims 20 to 26, wherein the caramel comprises purified caramel.

28. The product of Claim 27, wherein the caramel was purified by diafiltration and is the resulting retentate.

29. The product of Claim 28, wherein the resulting caramel retentate comprises no more than 30% of the mass of the unpurified caramel.

30. The product of Claim 28 or 29, wherein the caramel retentate is the material retained when passing untreated caramel through a membrane designated to have a molecular weight cut-off of from 2,000 to 30,000.

31. The product of Claim 28, 29 or 30, wherein a 0.1% solution of the purified caramel has an absorbance of from about 1.20 to 1.50 at 610 nanometers using a 1 cm cell.

32. The product of Claim 27, wherein the caramel is purified by triturating the caramel with ethyl alcohol and water.

33. The product of any one of Claims 21 to 25 or 27-32, wherein the carmine solution comprises from about 1.0% to 10% by weight of the dye.

34. A dye for colouring cigarette wrapper paper a rich brown colour comprising caramel as the brown colouring agent, a plasticiser to prevent the paper from becoming brittle, and water.

35. A process for purifying caramel colour extract substantially as hereinabove described with reference to Figures 1 or 2 of the drawings hereof.

36. A caramel retentate produced substantially as described hereinabove with reference to Example I, II, III or IV hereof.